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THE EFFECT OF A HIGH-VOLTAGE PULSE DISCHARGE ON THE CRYSTAL LATTICE AND THE SURFACE OF QUARTZ GRAINS

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The effect of a high-voltage pulse discharge on the crystal lattice and the surface of quartz grains is studied for different values of the energy input into the interelectrode space, the pulse duration, and the energy input rate. The reasons for the processes of activation of the quartz grain surface and the modification of the crystal lattice of quartz are accounted for. Practical recommendations are issued.

The progress and implementation of electron-ion pulse technologies contributes to improving the product quality and solving the problems of energy saving and environmental safety in technological processes. A variety of these technologies is the one in which the working instrument is a high-voltage discharge in liquid media. The electrohydrodynamic and electric pulse technologies of destruction of solid bodies are now well known.

The electric pulse technology developed at the Tomsk Polytechnic University has found application in drilling of wells, crushing ore, and breaking ferroconcrete waste generated in the course of production or after service [1 – 3].

Electric-pulse crushing differs from mechanical crushing, as is involves a complex set of factors accompanying the breakdown of a dielectric in a liquid medium, namely, the primary pressure waves from the expansion of the breakdown channel, the secondary pressure waves formed in the collapse of the steam-gas field, high plasma temperatures, and electromagnetic fields. In this process a substantial energy input (70 – 1000 J) is made into the interelectrode space within a short time interval ($10^{-4} - 10^{-9}$ μsec). Such intense energy impact ought to affect not only the formation of an active surface on the particles destroyed, but also the modification of the crystal lattice in the volume of solid bodies, in particular, of silicate minerals.

Quartz was chosen as the object of an electric pulse discharge. Quartz is a good model object and at the same time is used in different technologies.

The samples subjected to crushing were lumps of vein quartz from the Chupinskoe deposit with a high degree of purity (wt.%): 99.95790 SiO_2, 0.00079 TiO_2, 0.00530 Al_2O_3, 0.00036 MgO, 0.00850 CaO, 0.00800 Na_2O, and 0.00560 K_2O.

The pulse crushing of quartz was performed in various conditions: the pulse duration and the magnitude of the energy introduced into the interelectrode space varied. At the same time, the energy input rate varied from 24×10^6 to 134×10^6 J/sec. The parameters of pulse crushing and the surface properties of the products of crushing (fraction of 0.5 – 0.5 mm) of the Chupinskoe deposit quartz are listed in Table 1.

It is experimentally determined [4] that an impact-wave effect on amorphous silica at a pressure up to 28 GPa results in the formation of a cubic modification of SiO_2 of density 2.52×10^3 kg/m^3. The destruction of quartz with a high-voltage pulse discharge involves a shock-wave effect, which does not preclude a modification of the crystal lattice of quartz.

Quartz lumps sized 50 – 100 mm were subject to crushing to a particle size below 2 mm, which was provided by the size of the openings in the lower electrode of the high-voltage crushing chamber. After crushing, the surface properties of the particles of the products and the parameters of the crystal lattice of quartz were estimated. Furthermore, the

TABLE 1

Regime*	Parameters of electric pulse crushing			Properties of quartz surface	
	pulse duration, 10^{-6} sec	input energy, J	energy input rate, 10^6 J/sec	specific surface area, m^2/g	specific solubility in water, 10^{-4} μg/m^2
EPC-1	3.7	88	24	0.15	1.8
EPC-2	4.7	128	27	0.15	1.4
EPC-3	3.7	438	118	0.07	3.5
EPC-4	4.8	644	134	0.07	2.4
MC	–	–	–	0.11	1.3

* EPC) electric pulse crushing; MC) mechanical crushing.

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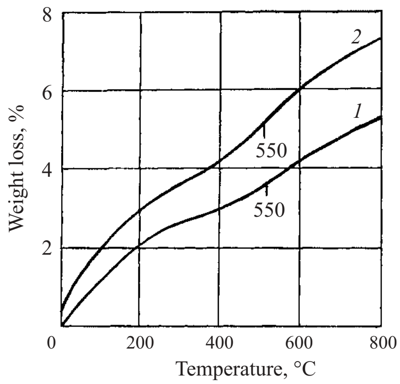

Fig. 1. Weight loss in heat treatment of Chupinskoe quartz (fraction 0.25 – 0.50 mm): *1*) mechanical crushing in water; *2*) electric-pulse crushing in water (regime EPC-3).

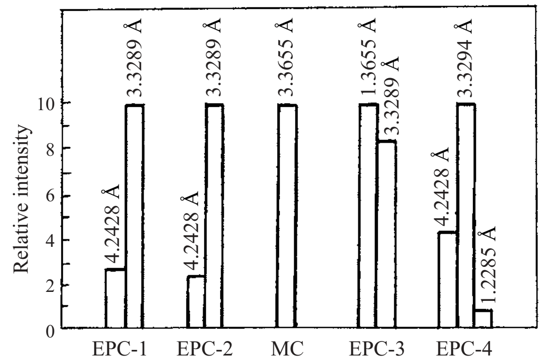

Fig. 2. The intensity of the characteristic x-ray diffraction maxima of quartz after mechanical and pulse crushing (fraction 0.25 – 0.50 mm).

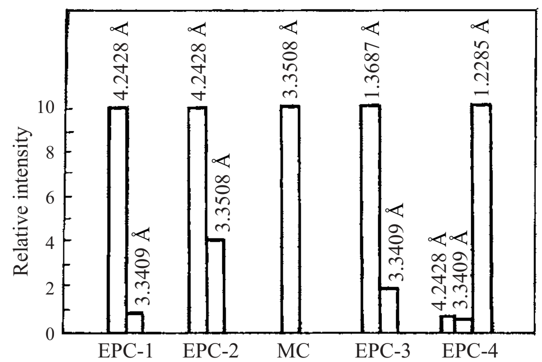

Fig. 3. Intensity of the characteristic x-ray diffraction maxima of quartz after mechanical dispersion of the products of crushing (to dispersion of 60 μm).

DTA method was used to register the shift in the temperature of the β-quartz → α-quartz phase transformation. For reference purposes, similar studies were performed on Chupinskoe quartz subjected to mechanical crushing. Mechanic grinding was primarily performed in a jaw crusher and then in an aqueous medium inside a metal mortar with separation of the required fractions from the product of crushing.

The quartz samples analyzed were the fraction 0.25 – 0.50 mm separated from the respective products of crushing. Some differences were identified in the surface properties of the quartz particles subjected to mechanical and pulse crushing. They include inadequate solubility of quartz in hydrofluoric acid depending on the specific surface area: as the specific surface area decreases, the solubility of quartz increases. Furthermore, water sorption was different in the quartz particles after mechanical and pulse crushing (Fig. 1). It was higher in particles subjected to pulse crushing. At the same time, the specific surface area of particles after pulse crushing is perceptibly smaller, and this tendency decreases as the energy input rate increases (Table 1). This suggests an effect of the high-voltage discharge on the crystal lattice of quartz.

All four oxygen atoms in the tetrahedra in the total volume of quartz are bridge atoms. Crushing facilitates liberation of the oxygen bond, which results in the formation of hydrate forms of the Si – O – H type on the surface [5].

The effect of pulse breakdown on the structure of a solid body is virtually unstudied.

Using the x-ray analysis we analyzed the structure of the crystal lattice of Chupinskoe quartz under the effect of a high-voltage pulse discharge with a variable input of energy into the interelectrode space per time unit. The analysis of the x-ray patterns demonstrated that a perceptible redistribution of the intensities of x-ray diffraction maxima and a modification of the position of the main maximum were registered in all cases of pulse crushing (Fig. 2). For crushing regimes with energy input rate $(24 – 227) \times 10^4$ J/sec (EPC-1, EPC-2), the main maximum is shifted to smaller angles ($d = 4.24$ Å) compared with the main maximum of the x-ray diffraction pattern of quartz after mechanical crushing ($d = 3.35$ Å). With an energy input rate greater than 118×10^6 J/sec (EPC-3, EPC-4), the intensity of the 3.3289 Å line increases but the 1.3655 Å reflection remains the most intense.

Treatment of the product of quartz crushing at a temperature or 105°C does not lead to a modification of the diffraction patterns. The diffraction patterns of the products of crushing at a temperature over 570°C differ both from the

TABLE 2

Elementary cell parameters of quartz	Crushing method				
	mechanical in water	mechanical in water, heat treatment at 570°C	electric pulse crushing (EPC-3)	products of EPC-3 after heat treatment at 570°C	quartz lattice [7]
a, ± 0.0002 Å	4.90015	4.90015	4.89950	4.90840	4.90430
c, ± 0.0002 Å	5.39180	5.39180	5.39920	5.39080	5.39740
V, Å^3	336.3631	336.3631	336.7354	337.4343	337.2800

TABLE 3

Quartz	Density, 10^{-3} kg/m^3			
	pycnometric*	pycnometric after grinding**	x-ray*	x-ray* after calcination at 570°C
Mechanical crushing	2.7297	2.6680	2.6659	2.6659
Electric pulse crushing (EPC-3)	2.6631	2.6623	2.6629	2.6574

* Grain size 0.25 – 0.50 mm.

** Dispersion more than 60 μm.

initial pattern after pulse crushing and from the reference pattern. The β-quartz → α-quartz modified transformations facilitate relaxation, and the diffraction pattern approaches the reference standard. A relaxation occurs as well in mechanical dispersion of the products of crushing (Fig. 3). This is corroborated by the calculation of the parameters of the crystal lattice of β-quartz (Table 2). As can be seen, a pulse discharge leads to a compression of the lattice in the parameter *a* and stretching in the parameter *c*, which on the whole produces a small increment of the crystal lattice volume compared to that of quartz after mechanical crushing. The pycnometric density of the pulse-crushed quartz is lower than that of mechanically crushed quartz (Table 3).

The quartz (Karelslyuda Concentration Works) from the Chupinskoe deposit contains gas inclusions and impurities of Al^{3+}, Na^+, K^+, and other ions; Al^{3+} replaces silicon in the tetrahedron, and the excess negative charge is compensated by Na^+ and K^+ ions [6]. These impurities determine the initial defects in quartz. The high-voltage pulse breakdown and the deformation of the crystal lattice should contribute to the removal of structural impurities, including gas inclusions, and the removal of Al^{3+} and K^+ loosens the structure (a low pycnometric density, DTA curves in Fig. 4). Calcination at the temperature of the β-quartz → α-quartz phase transformation (570°C) facilitates the restoration of the quartz structure to a state nearing the reference standard.

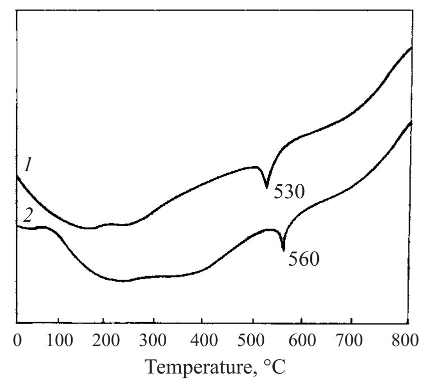

Fig. 4. DTA curves of the products of mechanical (*1*) and electric-pulse (*2*, EPC-3) crushing (fraction 0.25 – 0.50 mm).

Thus, all modes of pulse crushing activate the surface of quartz grains. A modification of the state of the crystal lattice is manifested at a certain rate of energy input into the space between the electrodes. The electric-pulse crushing method can be used in the preparation of quartz grit for producing quartz glass and in crushing substandard single quartz crystals in the case of recycling. This has been confirmed in industrial testing.

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